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# Processing of Alumina-Toughened Zirconia Composites

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# Processing of Alumina-Toughened Zirconia Composites

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Dense and crack-free 10-mol%-yttria-stabilized zirconia (10YSZ)-alumina composites, containing 0 to 30 mol% of alumina, have been fabricated by hot pressing. Release of pressure before onset of cooling was crucial in obtaining crack-free material. Hot pressing at 1600 °C resulted in the formation of ZrC by reaction of zirconia with grafoil. However, no such reaction was observed at 1500 °C. Cubic zirconia and  $\alpha$ -alumina were the only phases detected from x-ray diffraction indicating no chemical reaction between the composite constituents during hot pressing. Microstructure of the composites was analyzed by scanning electron microscopy and transmission electron microscopy. Density and elastic modulus of the composites followed the rule-of-mixtures. Addition of alumina to 10YSZ resulted in lighter, stronger, and stiffer composites by decreasing density and increasing strength and elastic modulus.

## Introduction

Solid oxide fuel cells (SOFC)<sup>1</sup> are being developed for various applications in the automobile, power generation, aeronautic, and other industries. More recently, NASA has explored the possibility of using SOFCs for aero-propulsion under its Zero Carbon Dioxide Emission Technology (ZCET) Project in the Aerospace Propulsion and Power Program. Yttria-stabilized zirconia (YSZ) is a very good anionic conductor at high temperatures, and is therefore used as an oxygen solid electrolyte in SOFC. It has high thermal expansion coefficient, low thermal shock resistance, low fracture toughness and poor mechanical strength, which may be sufficient for land-based power generation SOFC systems without thermal cycling. However, for aeropropulsion applications, the thin ceramic electrolyte membrane of the SOFC needs to be stronger and tougher as it would be subjected to thermal cycling and severe vibration forces during take off and landing. We are currently investigating the possibility of reinforcement of YSZ with alumina in order to enhance the strength and fracture toughness of the electrolyte, without degrading its electrical conductivity to an appreciable extent. This concept would also find applications in other industries such as the oxide ceramic cutting tools. Alumina is known to be an effective additive<sup>2</sup> for scavenging the resistive SiO<sub>2</sub> phase, present as impurities in the starting YSZ material, by removing it from grain boundaries. A limited solubility of alumina in YSZ<sup>3</sup> results in substitution of Al<sup>3+</sup> for Zr<sup>4+</sup> in the lattice and assists in sintering.<sup>4</sup> Additions of alumina also inhibit the grain growth in YSZ.

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The primary objective of this study was to develop the processing of 10YSZ composites reinforced with various concentrations of alumina. Dense and crack free 10YSZ-alumina composites, containing 0 to 30 mole percent of alumina, were fabricated. Microstructure, density, and room temperature mechanical properties of these composites are also reported here.

### Experimental

The starting materials used were alumina powder (Baikalox CR-30, 99.99% purity, average particle size 0.05  $\mu\text{m}$ , specific surface area 25  $\text{m}^2/\text{g}$ ) from Baikowski International Corporation, Charlotte, NC and 10 mol% yttria fully-stabilized zirconia powder (HSY-10, average particle size 0.41  $\mu\text{m}$ , specific surface area 5.0  $\text{m}^2/\text{g}$ ) from Daiichi Kigenso Kagaku Kogyo Co., Japan. Various steps involved during processing of the composite panels are shown in the flow chart of Fig. 1. Appropriate quantities of alumina and zirconia powders were slurry mixed in acetone and ball milled for ~24 h using zirconia milling media. Acetone was evaporated and the powder dried in an electric oven. The resulting powder was loaded into a graphite die and hot pressed in vacuum under 30 MPa pressure either into 1-in.-diameter discs using a mini-hot press or into 6 in. by 6 in. plates using a large hot press. Grafoil was used as spacers between the specimen and the punches. Various hot pressing cycles were tried in order to optimize the hot pressing parameters, which would result in dense and crack free ceramic samples. The hot pressed plates were machined into bend bars for flexure strength measurements. The sharp edges of test specimens were chamfered to reduce spurious premature failure emanating from those sharp edges.

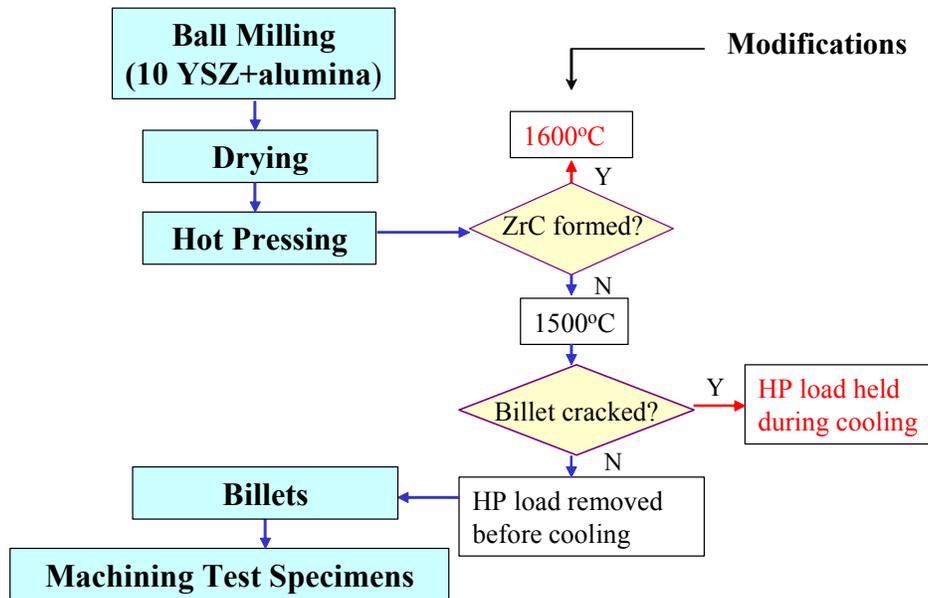


Figure 1. Flow chart showing various steps in the processing of dense and crack-free 10YSZ-alumina composites

X-ray diffraction (XRD) patterns were recorded at room temperature using a step scan procedure (0.02°/2θ step, time per step 0.5 or 1 s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing Cu K<sub>α</sub> radiation. Density was determined from weight and volume of each specimen. Elastic modulus was measured at room temperature using an impulse excitation method (Grindosonic) in accordance with ASTM test standard C-1259. Room temperature flexure strengths of the YSZ/alumina composites were determined in air using 50 by 4.0 by 3.0 mm bend bars in accordance with ASTM test standard C-1161.<sup>5</sup> Stress-strain curves were recorded using a four-point bend fixture having 40 mm outer span and 20 mm loading span, in conjunction with an electromechanical testing machine (Model 8562, Instron, Canton, MA). A fast stress rate of 50 MPa/s was applied in load control to reduce slow crack growth effect of the materials. A total of 10 test specimens were tested for each composite. A limited fractographic analysis was performed optically to examine fracture origins and their nature. Microstructures of the polished cross-sections were observed in a JEOL JSM-840A scanning electron microscope (SEM). Thin foils for transmission electron microscopy (TEM) were prepared using a procedure that involved slicing, polishing, and argon ion beam milling. The thin foils were examined in a Philips EM-400T operating at 120 keV. A thin carbon coating was evaporated onto the TEM thin foils and SEM specimens for electrical conductivity prior to analysis. X-ray element analyses of the phases were carried out using a Kevex Delta thin window energy dispersive spectrometer (EDS) and analyzer.

## Results and Discussion

XRD patterns from zirconia discs hot pressed for 1 h at 1500 or 1600 °C are shown in Fig. 2. The material hot pressed at 1500 °C shows the presence of only cubic-ZrO<sub>2</sub> whereas small amount of ZrC is also detected in the 1600 °C hot-pressed material. Formation of ZrC occurs from the reaction between zirconia and grafoil during hot pressing:



To avoid this reaction, all further hot pressing was done at 1500 °C. During initial runs, the pressure was released after the panel had cooled to ambient temperature. This resulted in badly cracked composite panels. On cooling from 1500 °C to room temperature under applied load, large residual stresses are produced due to large CTE of cubic zirconia which result in cracking. However, modification of the hot pressing cycle, where applied load was released before onset of cooling, alleviated the cracking problem.

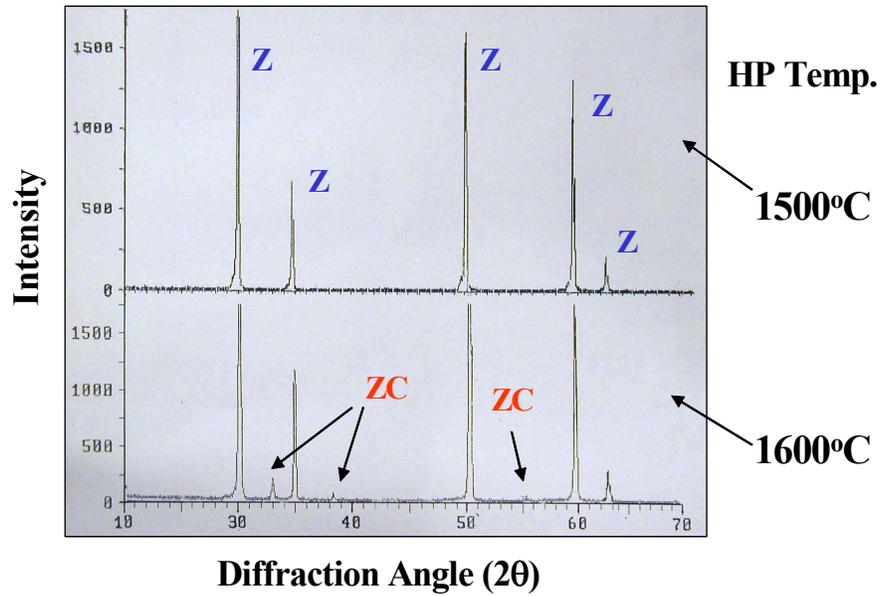


Figure 2. X-ray diffraction patterns of 10YSZ material hot pressed at 1500 °C and 1600 °C. Z and ZC indicate cubic-zirconia and zirconium carbide, respectively.

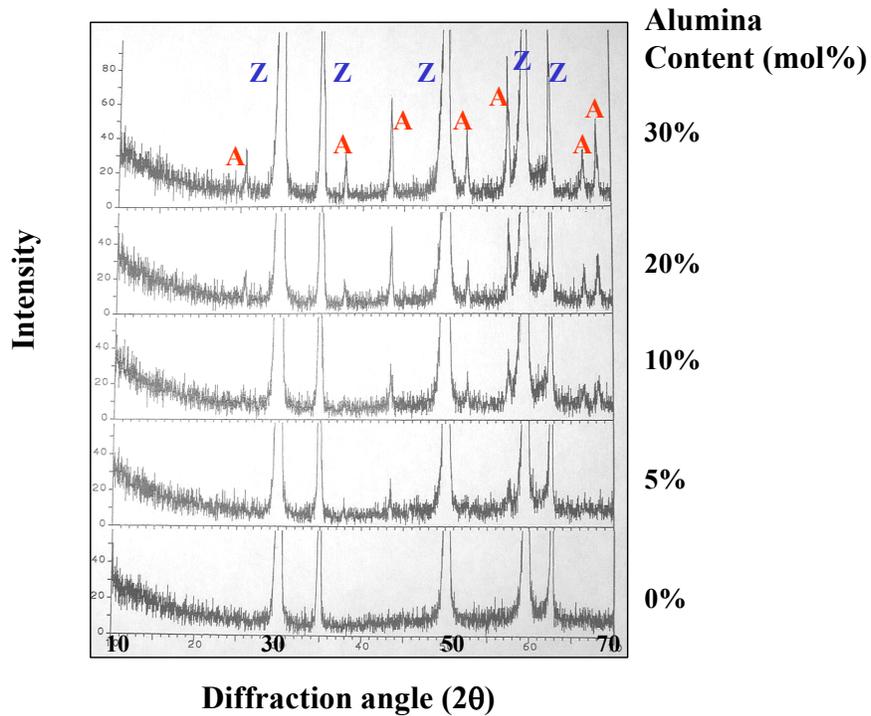


Figure 3. X-ray diffraction patterns for 10YSZ reinforced with different alumina contents. “Z” and “A” indicate *cubic-zirconia* and  $\alpha$ -alumina, respectively.

X-ray diffraction patterns from various 10YSZ-alumina composites containing 0 to 30 mol% alumina are shown in Fig. 3. Cubic zirconia and  $\alpha$ -alumina were the only phases present indicating the absence of any reaction between the materials during hot pressing at elevated temperatures. Typical SEM micrographs taken from polished cross-sections of various YSZ/alumina composites are shown in Figure 4. Alumina particulates are uniformly dispersed throughout the material. The dark areas represent alumina while the light areas indicate the

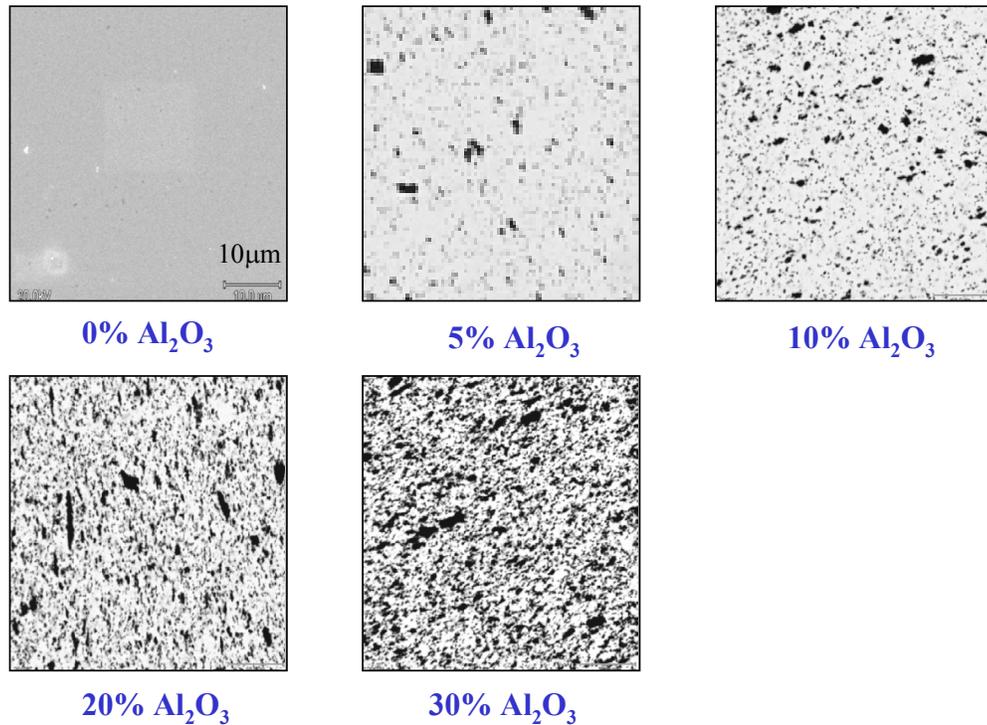


Figure 4. SEM micrographs showing polished cross-sections of 10YSZ-alumina composites containing various alumina mol%: (a) 0 mol%; (b) 5 mol%; (c) 10 mol%; (d) 20 mol%; (e) 30 mol%.

10YSZ matrix, as confirmed from EDS analysis (Fig. 5). TEM micrograph and dot maps for various elements for the composite containing 30 mol% alumina are shown in Fig. 6. The average equiaxed grain size is less than 1.0  $\mu\text{m}$  for either YSZ matrix or alumina. The high magnification TEM micrographs showing grain boundaries and triple junctions for the 0 and 30 mol% alumina composites are presented in Fig. 7 and 8, respectively. The grain boundaries as well as the triple junctions are clean for either the 0 or 30 mol% composite. Presence of any amorphous phase was not detected. No appreciable deformation or microcracks of adjacent

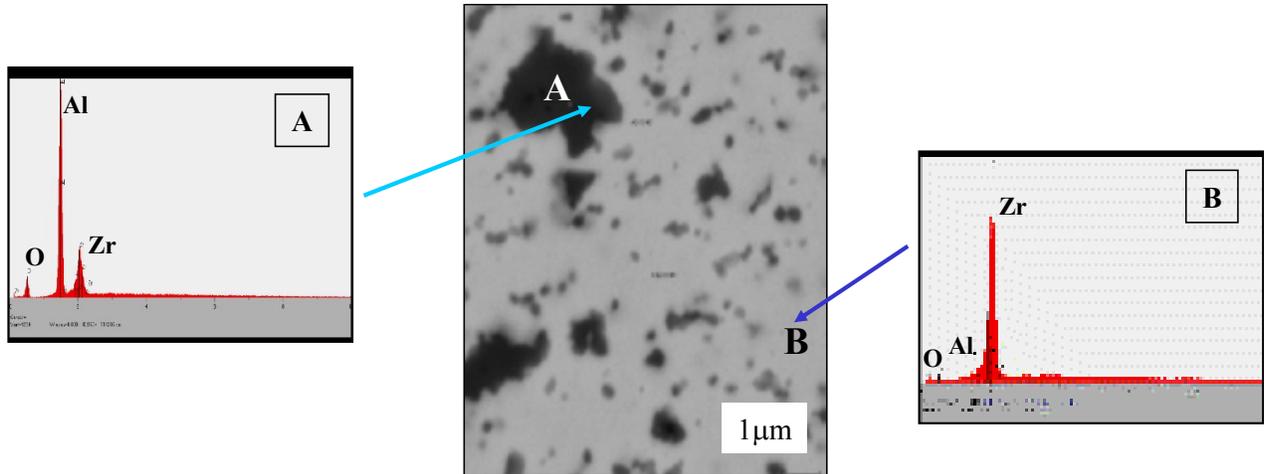


Figure 5. SEM micrograph and EDS analysis of 10YSZ-alumina composite containing 10 mol% alumina; dark area (A): alumina, light area (B): zirconia.

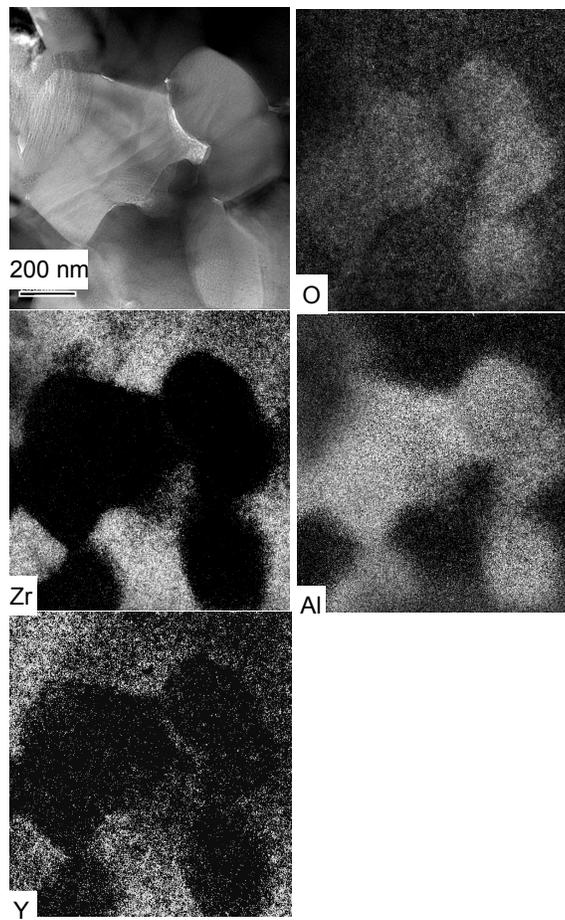
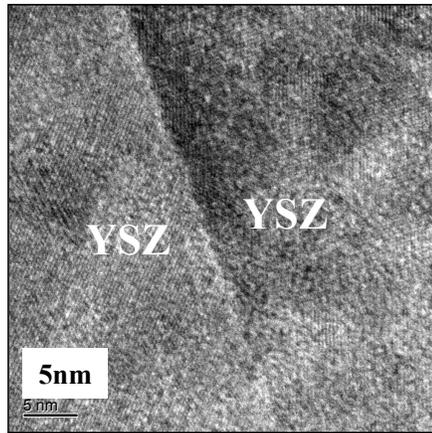
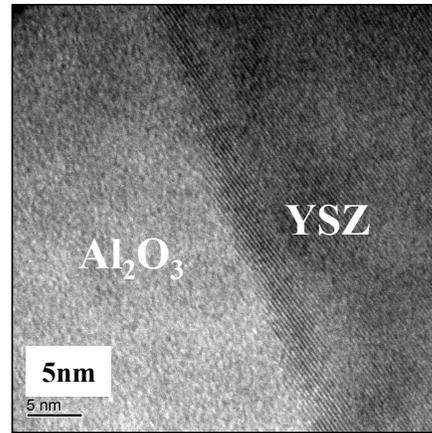


Figure 6. TEM micrograph showing zirconia and alumina grains and dot maps of different elements for 10YSZ-alumina composite containing 30 mol% alumina.

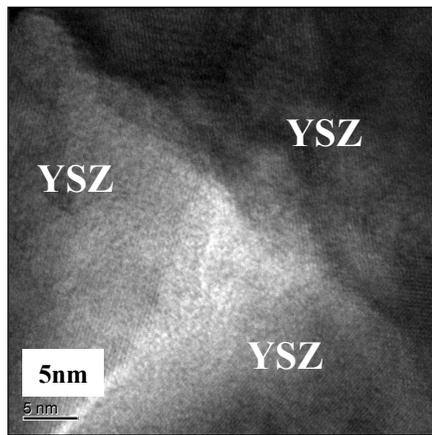


**0 mol% Al<sub>2</sub>O<sub>3</sub>**

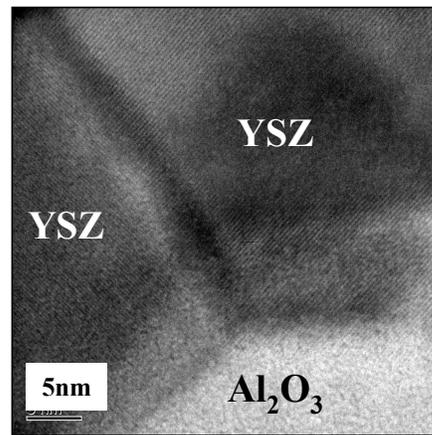


**30 mol% Al<sub>2</sub>O<sub>3</sub>**

Figure 7. High magnification TEM micrographs showing grain boundaries in 10YSZ-alumina composites containing 0 or 30 mol% alumina.



**0 mol% Al<sub>2</sub>O<sub>3</sub>**



**30 mol% Al<sub>2</sub>O<sub>3</sub>**

Figure 8. High magnification TEM micrographs showing triple junctions in 10YSZ-alumina composites containing 0 or 30 mol% alumina.

grains in the composites, which might occur due to thermoelastic mismatches between the YSZ matrix and the alumina particulates, was observed from the analysis of TEM micrographs.

Densities of 10YSZ-alumina composites as a function of mol% of alumina are presented in Table I and Fig. 9. Density,  $\rho$ , decreased with alumina content, as expected. The measured values were in agreement with those calculated from the rule-of-mixtures:

$$\rho_c = \rho_z V_z + \rho_A V_A \quad (2)$$

where  $V$  is the volume fraction and the subscripts  $c$ ,  $z$ , and  $A$  refer to the composite, zirconia and alumina, respectively. Values of  $\rho_z = 5.84 \text{ g/cm}^3$  and  $\rho_A = 3.85 \text{ g/cm}^3$  were used. Values of room temperature elastic modulus for various composites are listed in Table I and also shown in Fig. 10.

**Table I. Room Temperature Properties of 10YSZ-Alumina Composites**

Composite No.	Composition (mol%)		Density, $\rho$ ( $\text{g/cm}^3$ )	Elastic modulus $E$ (GPa)	Flexure strength $\sigma$ (MPa)
	10 YSZ	$\text{Al}_2\text{O}_3$			
A2-0	100	0	$5.839 \pm 0.008$	$219 \pm 2$	$280 \pm 23$
A2-5	95	5	$5.740 \pm 0.012$	$225 \pm 2$	$288 \pm 57$
A2-10	90	10	$5.642 \pm 0.007$	$233 \pm 1$	$319 \pm 64$
A2-20	80	20	$5.437 \pm 0.005$	$250 \pm 1$	$358 \pm 42$
A2-30	70	30	$5.178 \pm 0.042$	$262 \pm 1$	$393 \pm 38$

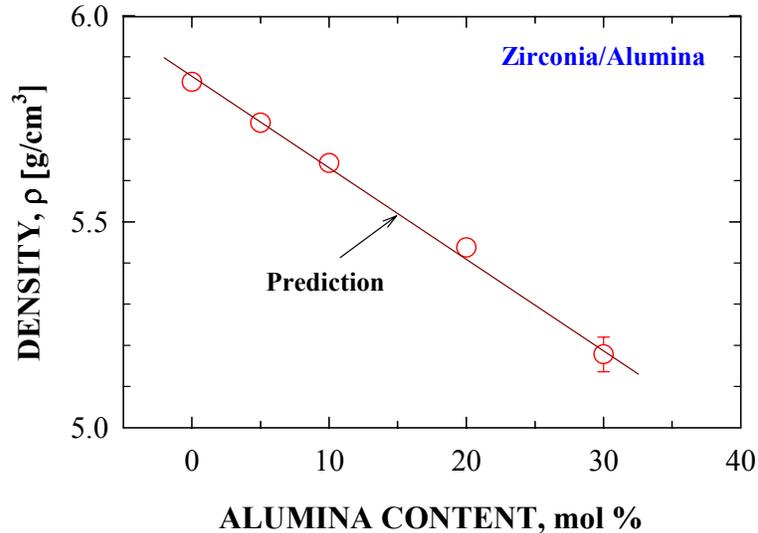


Figure 9. Density of 10YSZ-alumina composites as a function of alumina content. Solid line is prediction from rule-of-mixtures.

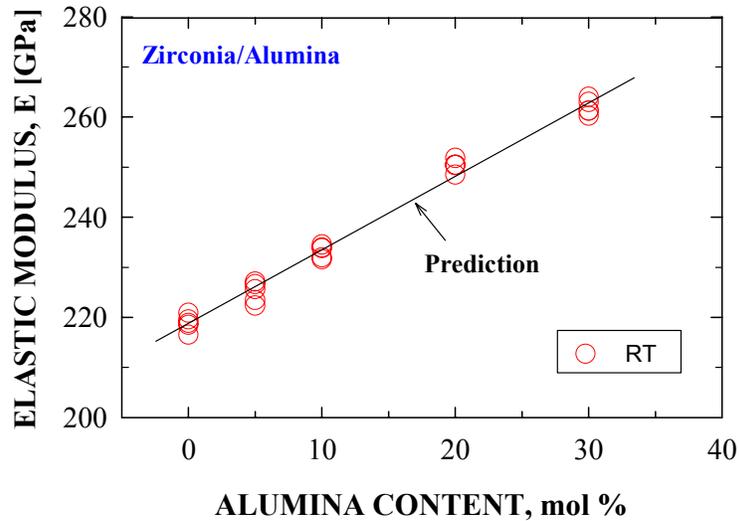


Figure 10. Room temperature elastic modulus of 10YSZ-alumina composites as a function of alumina content. Solid line is prediction from rule-of-mixtures.

Elastic modulus,  $E$ , increased with alumina content and the experimental values followed those calculated from the rule-of-mixtures

$$E_c = E_z V_z + E_A V_A \quad (3)$$

where  $V$  is the volume fraction and the subscripts  $c$ ,  $z$ , and  $A$  refer to the composite, zirconia and alumina, respectively. Values of  $E_z = 220$  GPa and  $E_A = 370$  GPa were used.

Room temperature flexure strength as a function of alumina (mol%) content for the 10YSZ-alumina composites are listed in Table I and also shown in Figure 11. The strength increased with increasing alumina content. The 30 mol% alumina composite showed 40% higher strength than the 10YSZ baseline material. The number of test specimens, 10 for each composition, was not sufficient to obtain the reliable Weibull statistical parameters such as Weibull modulus and characteristic strength. Weibull modulus that was estimated with 10 specimens, however, was found to be in the range of 5 to 15, typical of many commercial ceramics.

Typical examples of fracture surfaces of 10YSZ-alumina composites containing 0 and 30 mol% alumina, tested at ambient temperature, are shown in Figure 12. Fracture originated distinctly from surface-connected defects (“surface flaws”), associated with voids in conjunction

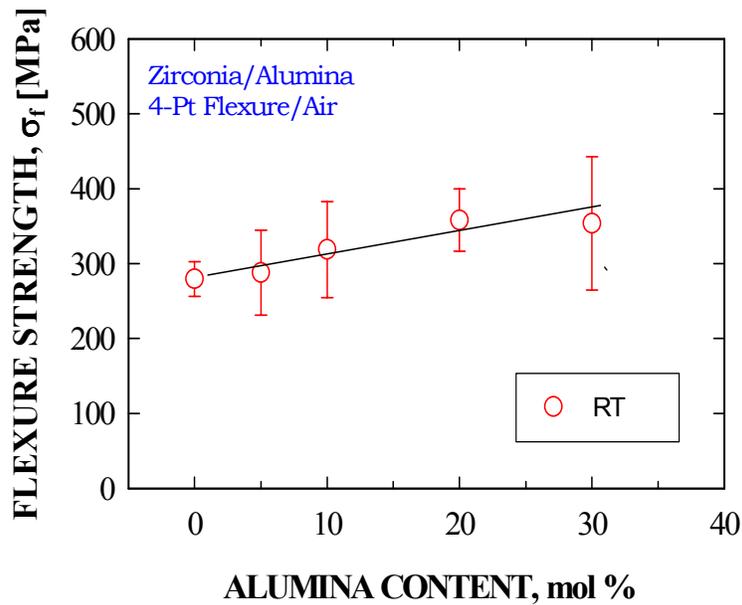
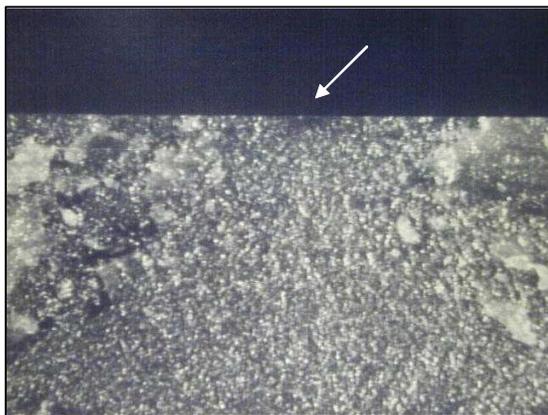


Figure 11. Room temperature flexure strength of 10YSZ-alumina composites as a function of alumina content in air. Error bars indicate  $\pm 1.0$  standard deviation. The line represents the best fit.



**0% alumina (RT)**



**30 mol% alumina (RT)**

Figure 12. Typical examples of fracture surfaces showing fracture origins (surface flaws indicated with arrows) for 10YSZ-alumina composites reinforced with (a) 0 mol% and (b) 30 mol% alumina.

with machining. Voids, contaminations and severity of machining were found to be dominant strength controlling surface flaws, independent of alumina content. Overall flaw sizes seemed to range from 20 to 40  $\mu\text{m}$ . Some other zirconia/alumina composites exhibited a strength decrease with increasing alumina content.<sup>7</sup> The strength decrease would be more significant for larger alumina particulates since they may act as strength-controlling flaws. On the contrary, fracture toughness in this case would be increased due to more enhanced crack deflection/bridging.

Temperature dependence of strength, fracture toughness, elastic modulus, coefficient of thermal expansion, thermal conductivity, and electrical ionic conductivity of zirconia-alumina composites will be reported elsewhere.<sup>8</sup>

### Summary and Conclusions

Dense and crack free 10YSZ-alumina composites containing 0 to 30 mol% alumina have been fabricated by hot pressing. Cubic zirconia and  $\alpha$ -alumina were the only phases present in hot pressed composites indicating no chemical reaction between the constituent materials during high temperature processing. Microstructure analysis of the composites was done using x-ray diffraction, SEM, TEM, and EDS. Density, elastic modulus and flexure strength of the composites were measured. Addition of alumina to 10YSZ resulted in lighter, stronger, and stiffer composite materials.

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